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Citation for final published version:

Galaverna, Renan, Fernandes, Lucas P., Browne, Duncan L. ORCID: <https://orcid.org/0000-0002-8604-229X> and Pastre, Julio C. 2018. Continuous flow processing as a tool for the generation of terpene-derived monomer libraries. Reaction Chemistry and Engineering 4 (2) , pp. 362-367. 10.1039/C8RE00237A file

Publishers page: <http://dx.doi.org/10.1039/C8RE00237A>  
<<http://dx.doi.org/10.1039/C8RE00237A>>

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# Continuous flow processing as a tool for the generation of terpene-derived monomer libraries†

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We report the development of a continuous flow approach for the preparation of two bio-derived monomer libraries. A small range of terpenes (ocimene, myrcene,  $\alpha$ -terpinene,  $\alpha$ -phellandrene, isoprene, and farnesene) have been used as the base set for the library, with the first library derived from a Diels–Alder re-action with the platform chemical maleic anhydride. The second library requires the derivatization of the first through a hydrogenation reaction. The potential for scale-up of both libraries has been demonstrated, with the Diels–Alder process delivering 10.5 grams of the product in 3 hours and the hydrogenation process delivering 10 grams of the material in 16 hours.

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† Electronic supplementary information (ESI) available: Experimental methods and results from control experiments.

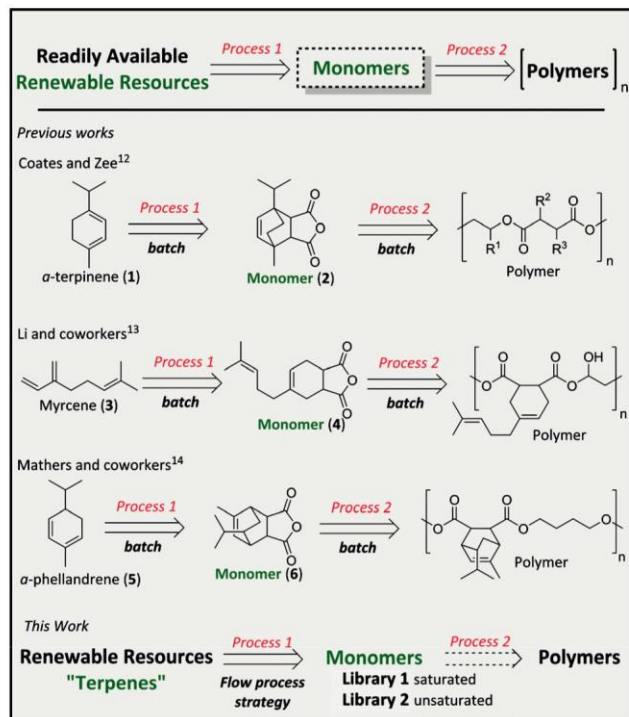
‡ R. G. and L. P. F. contributed equally to this work.

## Introduction

The conversion from fossil fuel-derived feedstocks to those derived from renewable resources is an ongoing pursuit with the progressive and evolving goal of delivering a more sus-tainable future. The growth of our modern society imposes increasing demands on depleting finite amounts of oil, gas and coal reserves, and it is estimated that these resources will be depleted by the end of the next century.<sup>1</sup> At this point, bio-mass presents a significant opportunity as a potentially sus-tainable source of organic carbon to meet our societal de-mands for the production of fuels, polymers and other essential materials.<sup>2</sup> Geared towards this change in feedstock supply, recent studies have demonstrated numerous chemi-cal transformation strategies to obtain bio-derived monomers and building blocks, which are of particular interest to us and this manuscript and some of these include polymers using terpenes as starting materials.<sup>3</sup>

Bio-based polymers derived from terpenes have already been the subject of several studies due to their relatively low cost; this important class of molecules is readily found in trees, flowers and fruits.<sup>4</sup> This class of molecules is varied in structure and may contain aliphatic and/or aromatic por-tions as well as C–C double bonds and other functional groups such as alcohols, aldehydes, ketones, esters and car-boxylic acids.<sup>5</sup> Owing to this structural diversity, a range of methodologies have been developed for the conversion of terpene-derived monomeric units into polymeric materials, such as cationic polymerization,<sup>6</sup> metathesis,<sup>7</sup> thiol–ene click chemistry,<sup>8</sup> condensation,<sup>9</sup> copolymerization,<sup>10</sup> and ring-opening polymerization.<sup>11</sup>

In addition to the development of polymerization reac-tions, the conversion of terpene starting materials into



Scheme 1 Terpene-based monomers to produce polymers.

monomeric units has also received attention (Scheme 1). For instance, Coates and Zee demonstrated the use of  $\alpha$ -terpinene (1) in the [4 + 2] cycloaddition reaction with maleic anhydride to prepare the corresponding monomer (2), which they copolymerized with propylene oxide to produce aliphatic polyesters with high glass transition temperatures.<sup>12</sup> The use of  $\alpha$ -phellandrene (5) was also explored in the latter study. Li and coworkers investigated the Diels–Alder reaction of myrcene (3) with maleic anhydride and demonstrated its use to produce vinyl ester resins (VER) in combination with tung oil.<sup>13</sup> Mathers and coworkers demonstrated the use of  $\alpha$ -phellandrene (5) and maleic anhydride to form the tricyclic monomer (6) by the Diels–Alder reaction, which was then polymerized by anhydride ring opening using diglycerol to form branched polyesters.<sup>14</sup> Whilst the reported processes focus on specific terpene-derived monomers and/or polymers, our own studies were designed to explore the use of continuous flow processing as a tool which would permit the more rapid scale-up synthesis of any materials of interest. Herein we report our findings on continuous processing for the synthesis of two small monomer libraries derived from terpene feedstocks.

Over the last decade, the use of continuous flow processing as a synthetic tool has started to become more common; this is partly attributable to several advantages that it can offer over batch processing (particularly at scale) such as improved heat and mass transfer, higher surface areas, suppressed hot spots, precise/rapid control of reaction parameters such as residence time, temperature and reactant stoichiometry, and the ability to couple with in-line monitoring and analytical techniques.<sup>15</sup> In the field of polymer science, several excellent contributions have been made using continuous flow processes with one of the main benefits be-

ing cited as high productivity.<sup>16</sup> Some recent approaches include carbocationic polymerization,<sup>17a</sup> organic photovoltaics by polycondensation,<sup>17b,c</sup> RAFT polymerization,<sup>17d–f</sup> ring-opening polymerization,<sup>17g</sup> and radical polymerization.<sup>17h</sup> Polypeptides have also been assembled under continuous flow conditions.<sup>18</sup>

## Results and discussion

### Part 1. Synthesis of unsaturated monomers by the Diels–Alder reaction in the flow regime

The initial evaluation of the strategy of producing monomers under flow conditions based on a Diels–Alder reaction started with the model reaction between  $\alpha$ -terpinene (1) and maleic anhydride (7). Initially, parameters such as the concentration, flow rate (residence time), and temperature were evaluated in order to achieve the optimal reaction conditions (Table 1). Guided by the principles of green chemistry, ethyl acetate (AcOEt) was chosen as a recommended green solvent for this study.<sup>19</sup>

Firstly, the concentration of the reaction was evaluated. The initial reaction provided 20 minutes of residence time at 90 °C and 0.25 M for combined streams afforded the Diels–Alder adduct (2) in 25% NMR yield (Table 1, entry 1). Increasing the concentration to 0.5 M and 1.0 M resulted in an increase in the observed yield to 34 and 70%, respectively (Table 1, entries 2 and 3). Increasing the concentration to 2.0 M was not possible due to the solubility of maleic anhydride. Proceeding with a 1 M concentration, the flow rate and reaction temperature were varied next, and the highest yield was achieved using 0.25 mL min<sup>−1</sup> at 140 °C (Table 1, entry 7). Under these conditions, the reaction mixture had 40 min residence time to achieve total conversion and delivered the desired monomer (2) in excellent yield (>95%).<sup>20</sup> In order to compare batch and flow processes, a batch reaction using the same concentration (1 M) and temperature (140 °C) was performed in a sealed tube. The difference between the flow process and the batch process for this Diels–Alder reaction is the three-fold longer reaction time under batch conditions (entry 9). Indeed, recent reports have demonstrated that these differences are mainly associated with the improved mixing and heat transfer properties of meso-scale flow reactors for Diels–Alder reactions.<sup>21</sup>

The optimum conditions for the model Diels–Alder reaction were then evaluated using a range of recommended green solvents.<sup>19</sup> For all seven of the assessed solvents (Table 1), the yields remained at >95%, demonstrating a robust process.

With the optimized Diels–Alder conditions in hand, the scope of this transformation in flow was evaluated using a small range of terpene inputs. For this purpose, myrcene (3),  $\alpha$ -phellandrene (5), ocimene (8), isoprene (9), farnesene (10) and non-terpene 1,3-cyclohexadiene (11) were investigated with ethyl acetate as the solvent. In this event, we were pleased to find that no blockage occurred across the sub-strate scope and isolated yields up to quantitative could be



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Julio C. Pastre joined the group of Professor Steven V. Ley at the University of Cambridge as a Postdoctoral Research Associate. Since 2014, he has been working as an Assistant Professor at UNICAMP and his general areas of interest focus on the development of new synthetic methods in batch and continuous-flow regimes for the synthesis of natural products, new materials, drugs and new drug candidates.



Table 1 Optimization of the continuous-flow Diels–Alder reaction between  $\alpha$ -terpinene (1) and maleic anhydride (7) using AcOEt as a reaction solvent

# Optimization

Reaction scheme showing the optimization of the Diels-Alder reaction. Reactant (1) in loop and (7) in loop are pumped into a 10 mL reactor at 10 bar and temperature  $\Delta$  °C. The product (2) is collected.

	C	Flow	r.t.	T	Conv <sup>a</sup>	Yield <sup>b</sup>
Entry	(mol L <sup>-1</sup> )	(mL min <sup>-1</sup> )	(min)	(°C)	(%)	(%)
1	0.25	0.5	20	90	27	25
2	0.5	0.5	20	90	36	34
3	1	0.5	20	90	73	70
4	1	0.5	20	110	80	76
5	1	0.25	40	110	95	92
6	1	0.166	60	110	98	93
7	1	0.25	40	140	100	>95
8	1	0.33	30	140	97	93
9 <sup>c</sup>	1	Batch	120	140	100	>95

## Solvent Screen

<b>AcOEt</b>	<b>ACN</b>	<b>Acetone</b>	<b>Anisole</b>
Conversion: 100%	Conversion: 100%	Conversion: 100%	Conversion: 100%
Yield: >95%	Yield: >95%	Yield: >95%	Yield: >95%
<b>MEK</b>	<b>Me-THF</b>	<b>MIBK</b>	
Conversion: 100%	Conversion: 100%	Conversion: 100%	
Yield: >95%	Yield: >95%	Yield: >95%	

<sup>a</sup> Conversion was determined by GC-MS. <sup>b</sup> Yields were determined by <sup>1</sup>H NMR using 1,3,5-trimethoxybenzene as the internal standard.

<sup>c</sup> Batch conditions:  $\alpha$ -terpinene solution in 1 M using AcOEt in a sealed tube at 140 °C.

achieved; the results are presented in Table 2. For all the terpenes addressed in flow, there was no requirement for reoptimization of the reaction conditions. The ocimene-derived monomer (12) presented the lowest yield (86%), attributable to the purity of the input; the commercially supplied material is a mixture of isomers in 90% purity (cis/ trans- $\beta$ -ocimene) along with 10% of other terpenes such as limonene and carene.

We were also pleased to find that the reaction could be readily scaled by simply switching the system from a segmented mode, using loading loops, to a continuous process-ing set-up capable of delivering 10.6 grams of the Diels–Alder adduct 2 (95% isolated yield) within 3 hours of processing translating to a productivity of 15 mmol h<sup>-1</sup> (3.54 g h<sup>-1</sup>). The result is presented in Table 2.

## Part 2. Synthesis of saturated monomers by sequential Diels–Alder/hydrogenation reactions in flow

For the second monomer library, we turned our attention to hydrogenation of unsaturated monomers using heterogeneous catalysts in flow. Indeed, heterogeneous catalysis has been well studied in mesoscale flow chemistry.<sup>22</sup> Several advantages are listed for heterogeneous flow methodologies, some of which include recyclability, ease of handling and improved safety.<sup>22</sup> In the flow process, the combination of

Table 2 Scope of monomers obtained by Diels–Alder reactions using various terpenes in flow and scale-up experiment

Entry <sup>a</sup>	Terpene	Product <sup>b</sup>
1	$\alpha$ -Terpinene (1)	2, 95%
2	Myrcene (3)	4, 93%
3	$\alpha$ -Phellandrene (5)	6, 91%
4	Ocimene (8)	12, 86%
5	Isoprene (9)	13, 99%
6	Farnesene (10)	14, 99%
7	Non-terpene, 1,3-cyclohexadiene (11)	15, 99%

Scale up experiment <sup>[c]</sup>	

<sup>a</sup> Flow reaction conditions: terpene (2 M in AcOEt) and maleic anhydride (2.2 M in AcOEt) were located in loops of 1 mL. A flow rate of 0.25 mL min<sup>-1</sup> was used at 140 °C, providing a residence time of 40 min. <sup>b</sup> Isolated yields. <sup>c</sup> Terpinene and maleic anhydride were directly pumped from the flask solution.

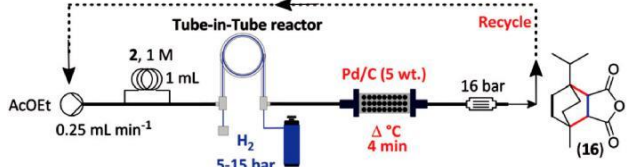
immobilized metal catalysts and hydrogen gas as the hydrogen source is the most common methodology for hydrogenation protocols. When gas–liquid–solid triphasic reactions take place in these systems, due to the high surface area of the microchannels, the diffusion and interaction among gas–

liquid–solid reagents are very efficient and not attainable in traditional batch processes (100-fold greater than batch).<sup>23</sup> As part of a recent development, tube-in-tube gas–liquid flow re-actors have been widely used for mesoscale applications. This technology was introduced by Ley and O'Brien et al., the reactor consists of two concentric tubes in which pressurized gas permeates through a semipermeable Teflon AF-2400 membrane and a broad range of gases have been investigated.<sup>24</sup> Some recent protocols using this tube-in-tube reactor include ozonolysis of alkenes,<sup>25</sup> carboxylation of Grignard reagents,<sup>26</sup> methoxycarboxylation,<sup>27</sup> dimethylaminocarbonylation,<sup>28</sup> hydroformylation,<sup>29</sup> Glaser–Hay coupling,<sup>30</sup> oxidative nitro–Mannich reactions,<sup>31</sup> Wacker oxidation,<sup>32</sup> synthesis of isothioureas,<sup>33</sup> synthesis of pyrroles,<sup>34</sup> asymmetric hydrogenation<sup>35</sup> and the scaled-up synthesis of the anti-inflammatory compound fentanyl.<sup>36</sup>

A range of heterogeneous metals was screened under batch conditions initially, to screen for the most selective and highest yielding catalyst for the effective alkene reduction of the D–A adduct (13) (see Table S1 of the ESI† for more details). It was found that palladium on carbon (Pd/C) provided the best selectivity (99%) and yield (99%) for hydrogenation in the batch process using a hydrogen gas cylinder as the hydrogen source. Amongst the undesired reactions for other metal catalysts was the ring opening of the anhydride to form diacid products. With this preliminary steer on the optimum catalyst, a glass column was packed with Pd/C and, initially, single-pass experiments were conducted under flow conditions (Table 3).

Notably, at 1 M concentration in alkene, single-pass hydrogenation reactions were ineffective (Table 3). Increasing the pressure of hydrogen gas from 5 to 15 bar resulted in a conversion increase from 2 to 10% (Table 3, entries 1–3) and heating the glass column to 70 °C led to no improvement (Table 3, entry 4). Since our attempts for single-pass experiments failed at the desired concentration and flow rates, we conducted a recycling experiment in order to achieve com-

Table 3 Heterogeneous catalysis for the hydrogenation reaction of monomer 2 in the flow regime<sup>a</sup>



Entry	Temperature (°C)	Residence time (min)	H <sub>2</sub> (bar)	Conv <sup>b</sup> (%)
1 <sup>c</sup>	r.t	4	5	2
2 <sup>c</sup>	r.t	4	10	5
3 <sup>c</sup>	r.t	4	15	10
4 <sup>c</sup>	70	4	15	4
5 <sup>d</sup>	r.t	330	15	100

<sup>a</sup> Column details: glass column (6.6 mm i.d. × 50.0 mm length)

packed with 750 mg of Pd/C (5% wt), void volume ca. 1 mL.

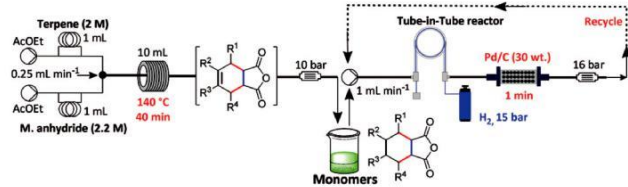
<sup>b</sup> Conversion was determined by GC-MS. <sup>c</sup> Single-pass experiment. <sup>d</sup> Reaction recycled through the system.

plete conversion to the reduced product (16). After 330 min of recycling the output back through the reactor using a flow rate of 0.25 mL min<sup>-1</sup>, complete conversion was observed (entry 5, Table 3). Although disappointing, we are somewhat encouraged that other studies have also had to adopt the necessary recycling strategy for flow hydrogenation protocols using Pd/C as the catalyst.<sup>22,37</sup>

Since both Diels–Alder and hydrogenation reactions were optimized, a sequential or multistep Diels–Alder/ hydrogenation protocol was evaluated in order to produce the unsaturated monomer library directly. For this purpose, in the first stage, the Diels–Alder reaction was performed at 0.25 mL min<sup>-1</sup> at 140 °C followed by heterogeneous hydrogenation in the second stage. For the hydrogenation part of the process, the flow rate was increased to 1 mL min<sup>-1</sup> and Pd/C 5% wt was replaced with 30% wt. In this context, all the terpenes were used in this set-up and the scope of the sequential process is presented in Table 4 (further details can be found in Fig. S1 of the ESI†).

All of the terpenes explored afforded excellent yields ranging from 80 up to 96%. Notably, the residence times for the recycling of the hydrogenation reaction were individually optimized and varied between 80 and 510 min, as might be expected given the differing levels of steric hindrance around the double bonds and indeed the number of double bonds

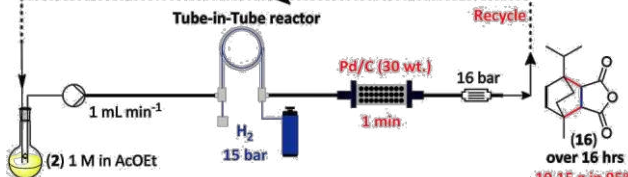
Table 4 Diels–Alder/hydrogenation and scale-up experiment in the flow regime<sup>a</sup>



Terpene	Yield (%)	Residence time (min)
α-terpinene	16, 95%	120 min
Myrcene	17, 96%	370 min
α-phellandrene	18, 91%	190 min
Ocimene	19, 80%	550 min
Isoprene	20, 96%	160 min
Farnesene	21, 96%	340 min
1,3-CHD	22, 94%	150 min

**Scale up experiment**



over 16 hrs  
10.15 g in 95%

<sup>a</sup> Column details: glass column (6.6 mm i.d. × 50.0 mm length) packed with 750 mg of Pd/C (30% wt), void volume ca. 1 mL.

present. For example, the monomers derived from myrcene (4), ocimene (12) and farnesene (14) present higher numbers of reducible bonds and correspondingly higher reaction times for the reduction to be complete (Table 4).

The reuse and reliability of the Pd/C hydrogenation catalyst were evaluated (leaching was not evidenced, see the ESI† for details), by comparing the performance against the benchmark hydrogenation of monomer 2 (from  $\alpha$ -terpinene). The benchmark optimal conditions afforded the reduced product 16 in 95% yield, and the same catalyst column was then used to optimize the hydrogenation of all other sub-strates before finally repeating the original benchmark and finding that the reaction time required for complete conversion remained the same (120 min).

Finally, we investigated the scale-up performance of the hydrogenation reaction of monomer 2 in flow. A stock solution containing 10 g of monomer 2 (43 mmol) was recirculated through the tube-in-tube reactor; a recirculating time of 16 hours was required for complete hydrogenation and afforded the hydrogenated monomer 16 (43 mmol, 10.15

g) in 95% isolated yield after simple removal of the solvent

by evaporation. Fig. S2 (ESI†) shows a comparison between the  $^1\text{H}$  NMR spectra of the isolated monomer 16 and that which was obtained from the crude reaction mixture of the scale-up experiment. Notably, there is a great similarity between the spectra, which have just an additional peak at 3 ppm attributable to succinic anhydride, the reduced form of maleic anhydride used in molar excess (1.1 equivalents) for the Diels–Alder reaction.

## Conclusions & outlook

In conclusion, we have developed a continuous flow process for the preparation of monomer libraries derived from renewable terpene feedstocks. The first library is secured through a Diels–Alder reaction which can be conducted in continuous flow. The second library is derived through the exhaustive hydrogenation of the alkenes present in the first library. The hydrogenation is achieved through the use of a Teflon AF-2400 tube-in-tube reactor and a Pd/C catalyst column in a recycle flow (or semi-batch) process. Notably, both of these processes can deliver multiple grams of the monomer units by simply by-passing the use of loading loops. Although the monomer libraries that have been demonstrated here are small in size, the gamut of polymerization reactions available to explore with them is encouraging (especially library 1 with two functional handles). For instance, compared to polymers containing acyclic monomer units, it is known that polymers formed from monomers with bicyclic rings can offer superior mechanical properties,<sup>38</sup> higher degrees of optical clarity<sup>39</sup> and higher  $T_g$  values.<sup>40</sup> Exploring continuous flow polymerization processes with these monomers is ongoing in our laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors gratefully acknowledge financial support from the São Paulo Research Foundation – FAPESP (J. C. P., awards No. 2014/26378-2 and 2014/25770-6), CNPq (J. C. P., award No. 453862/2014-4) and CAPES (R. G.). This project was also partly supported by seed funding from Cardiff University's allocation of the Higher Education Funding Council Wales GCRF QR Fund (D. L. B.).

## Notes and references

- I. Capellán-Pérez, M. Mediavilla, C. Castro, O. Carpintero and L. J. Miguel, *Energy*, 2014, 77, 641–666.
- (a) M. Graglia, N. Kanna and D. Esposito, *ChemBioEng Rev.*, 2015, 2, 377–392; (b) S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasik and P. T. Anastas, *Green Chem.*, 2017, 19, 4200; (c) A. Arevalo-Gallegos, Z. Ahmadb, M. Asgher, R. Parra-Saldivar and H. M. N. Iqbal, *Int. J. Biol. Macromol.*, 2017, 99, 308–318; (d) M. V. Galkin and J. S. M. Samec, *ChemSusChem*, 2016, 13, 1544–1558.
- (a) R. De Clercq, M. Dusselier and B. F. Sels, *Green Chem.*, 2017, 19, 5012–5040; (b) S. Choi, C. W. Song, J. H. Shin and S. Y. Lee, *Metab. Eng.*, 2015, 28, 223–239; (c) R. A. Sheldon, *Green Chem.*, 2014, 16, 950–963; (d) N. Mahmood, Z. Yuan, J. Schmidt and C. Xu, *Renewable Sustainable Energy Rev.*, 2016, 60, 317–329; (e) Y. Xia and R. C. Larock, *Green Chem.*, 2010, 12, 1893–1909.
- (a) P. A. Wilbon, F. Chu and C. Tang, *Macromol. Rapid Commun.*, 2013, 1, 8–37; (b) Y. Zhu, C. Romain and C. K. Williams, *Nature*, 2016, 540, 354–362.
- E. Breitmaier, *Terpenes: Importance, General Structure, and Biosynthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, 2006, p. 214.
- (a) W. Malte and R. Bernhard, *ChemSusChem*, 2015, 8, 2455–2471; (b) S. Kotaro, *Polym. J.*, 2015, 47, 527–536.
- (a) K. Shingo, L. Cheng, R. H. Thomas and A. H. Marc, *J. Am. Chem. Soc.*, 2009, 131, 7960–7961; (b) T. M. Robert, D. Krishnan, G. R. Matthew and S. L. Michael, *Macromolecules*, 2009, 42, 1512–1518.
- F. Maulidan, M. E. Lucas and A. R. M. Michael, *Macromolecules*, 2011, 44, 7253–7262.
- (a) B. Ioan and M. Fanica, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, 45, 5979–5990; (b) N. Nobuyoshi, Y. Nao, T. Ko and A. Keigo, *Macromolecules*, 2003, 36, 3007–3009.
- (a) L. An-Long, W. Xiao-Yan, L. Hui and L. Jiang, *React. Funct. Polym.*, 2007, 67, 481–488; (b) W. Yi, L. An-Long, L. Hui and L. Jiang, *Eur. Polym. J.*, 2006, 42, 2695–2702.
- (a) Z. Junpeng, S. Helmut, W. Steffen and A. Markus, *Polym. Chem.*, 2012, 3, 1763–1768; (b) W. Jifu, P. C. Yung, Y. Kejian, A. W. Perry, Z. Wujie, R. Lixia, Z. Juhua, N. Mitzi, W. Chunpeng, C. Fuxiang, H. Xiaoming, W. D. Alan and T. Chuanbing, *Chem. Commun.*, 2012, 48, 916–918.
- N. J. Zee and G. W. Coates, *Angew. Chem.*, 2015, 127, 2703–2706.
- X. Yanga, S. Li, J. Xia, J. Songa, K. Huang and M. Li, *Ind. Crops Prod.*, 2015, 63, 17–25.

- 14 (a) D. Dakshinamoorthy, A. K. Weinstock, K. Damodaran, D. F. Iwig and R. T. Mathers, *ChemSusChem*, 2014, 7, 2923–2929; (b) D. Dakshinamoorthy, S. P. Lewis, M. P. Cavazza, A. M. Hoover, D. F. Iwig, K. Damodaran and R. T. Mathers, *Green Chem.*, 2014, 16, 1774–1783.
- 15 (a) B. P. Matthew, P. Bartholomaeus, G. Kerry and H. S. Peter, *Chem. Rev.*, 2017, 117, 11796–11893; (b) K. S. Elvira, X. C. Solvas, R. C. R. Wootton and A. J. deMello, *Nat. Chem.*, 2013, 5, 905–915; (c) B. J. Reizman and K. F. Jensen, *Acc. Chem. Res.*, 2016, 49, 1786–1796; (d) J. M. Souza, R. Galaverna, A. N. Aline, T. J. Brocksom, J. C. Pastre, R. O. M. A. Souza and K. T. Oliveira, *An. Acad. Bras. Cienc.*, 2018, 90, 1131–1174; (e) I. M. Mándity, S. B. Ötvös and F. Fülöp, *ChemistryOpen*, 2015, 4, 212–223; (f) I. M. Mándity, S. B. Ötvös, G. Szőllősi and F. Fülöp, *Chem. Rec.*, 2016, 16, 1018–1033.
- 16 (a) T. Christoph, N. Adrian, L. Holger and F. Holger, *Macromolecules*, 2012, 45, 9551–9570; (b) T. Junkers and B. Wenn, *React. Chem. Eng.*, 2016, 1, 60–64; (c) A. Nagaki and J. Yoshida, *Advances in Polymer Science*, Springer, Cham, 2012, vol. 259; (d) W. Daniel, K. Johannes and F. Holger, *Macromol. Chem. Phys.*, 2008, 209, 343–356.
- 17 (a) A. Nagaki, K. Kawamura, S. Suga, T. Ando, M. Sawamoto and J.-i. Yoshida, *J. Am. Chem. Soc.*, 2004, 126, 14702–14703; (b) P. Geert, K. Jurgen, V. Pieter, G. Sanne, M. Jean, L. Laurence, V. Dirk and M. Wouter, *ChemSusChem*, 2015, 8, 3228–3233; (c) S. Helga, J. J. David, B. H. Andrew and W. H. W. Wallace, *Chem. Commun.*, 2012, 48, 1598–1600; (d) G. James, H. H. Christian, T. John and G. Duncan, *Eur. Polym. J.*, 2016, 80, 200–207; (e) R. Maarten, L. Phanumat and J. Tanja, *Polym. Chem.*, 2017, 8, 6496–6505; (f) H. H. Christian, G.-S. Carlos, B. Malte, S. Simon, C. John, M. Graeme, R. Ezio and H. T. San, *Org. Process Res. Dev.*, 2011, 15, 593–601; (g) H. Xin, Z. Ning, F. Zheng and G. Kai, *React. Chem. Eng.*, 2017, 2, 20–26; (h) L. R. Bonnie, M. P. Ryan, R. B. Logan and M. M. Garret, *Macromolecules*, 2017, 50, 2668–2674.
- 18 A. J. Mijalis, D. A. Thomas, M. D. Simon, A. Adamo, R. Beaumont, K. F. Jensen and B. L. Pentelute, *Nat. Chem. Biol.*, 2017, 13, 464–466.
- 19 P. Denis, P. Olivier, F. Hans-Wolfram, L. Sylvie, D. Véronique, I. Pascal, G. Eberhard, S. Thomas, R. Stéphane, C. Paul and H. Patrik, *Org. Process Res. Dev.*, 2013, 17, 1517–1525.
- 20 Notably, these conditions are similar to those reported for the conversion of myrcene: H. H. Christian, Á. Á-D. Miguel, M. K. Thomas and T. John, *Beilstein J. Org. Chem.*, 2017, 13, 120–126.
- 21 (a) S. Seghers, L. Protasova, S. Mullens, J. W. Thybaut and C. V. Stevens, *Green Chem.*, 2017, 19, 237–248; (b) A. Stefan, H. Stefan, S. Gunther, F. Jacques-Alexis and M. Roger, *Org. Process Res. Dev.*, 2012, 16, 1114–1120; (c) C. Valerio, B. Maurizio, C. Franco, P. Alessandra, A. Rita and C. Giuseppe, *Org. Lett.*, 2013, 15, 3590–3593; (d) I. Nekkaa, M. Palkó, I. M. Mándity and F. Fülöp, *Beilstein J. Org. Chem.*, 2018, 14, 318–324; (e) I. Nekkaa, M. Palkó, I. M. Mándity, F. Miklós and F. Fülöp, *Eur. J. Org. Chem.*, 2018, 32, 4456–4464.
- 22 (a) I. Muhammad, N. G. Toma and C. O. Kappe, *ChemSusChem*, 2011, 4, 300–316; (b) C. David and C. O. Kappe, *ChemCatChem*, 2014, 6, 3286–3305; (c) T. Abdulkadir, J. Stephan and A. Khalid, *Chem. Eng. J.*, 2017, 327, 792–821.
- 23 J. Kobayashi, Y. Mori and S. Kobayashi, *Chem. – Asian J.*, 2006, 1, 22–35.
- 24 B. Martin, M. O'Brien, S. V. Ley and A. Polyzos, *Acc. Chem. Res.*, 2015, 48, 349–362.
- 25 M. O'Brien, N. Taylor, I. R. Baxendale and S. V. Ley, *Org. Lett.*, 2010, 12, 1596–1598.
- 26 A. Polyzos, M. O'Brien, T. P. Petersen, I. R. Baxendale and S. V. Ley, *Angew. Chem., Int. Ed.*, 2011, 50, 1190–1193.
- 27 P. Koos, U. Gross, A. Polyzos, M. O'Brien, I. R. Baxendale and S. V. Ley, *Org. Biomol. Chem.*, 2011, 9, 6903–6908.
- 28 U. Gross, P. Koos, M. O'Brien, A. Polyzos and S. V. Ley, *Eur. J. Org. Chem.*, 2014, 6418–6430.
- 29 S. Kasinathan, S. L. Bourne, P. Tolstoy, P. Koos, M. O'Brien, R. W. Bates, I. R. Baxendale and S. V. Ley, *Synlett*, 2011, 18, 2648–2651.
- 30 T. P. Petersen, A. Polyzos, M. O'Brien, T. Ulven, I. R. Baxendale and S. V. Ley, *ChemSusChem*, 2012, 5, 274–277.
- 31 M. Brzozowski, J. A. Forni, G. P. Savage and A. Polyzos, *Chem. Commun.*, 2015, 51, 334–337.
- 32 S. L. Bourne and S. V. Ley, *Adv. Synth. Catal.*, 2013, 355, 1905–1910.
- 33 D. L. Browne, M. O'Brien, P. Koos, P. B. Cranwell, A. Polyzos and S. V. Ley, *Synlett*, 2012, 23, 1402–1406.
- 34 P. B. Cranwell, M. O'Brien, D. L. Browne, P. Koos, A. Polyzos, M. Peña-López and S. V. Ley, *Org. Biomol. Chem.*, 2012, 10, 5774–5779.
- 35 S. Newton, S. V. Ley, E. Casas Arce and D. M. Grainger, *Adv. Synth. Catal.*, 2012, 354, 1805–1812.
- 36 J. C. Pastre, D. L. Browne, M. O'Brien and S. V. Ley, *Org. Process Res. Dev.*, 2013, 17, 1183–1191.
- 37 (a) P. Albin and B. Jurka, *J. Hazard. Mater.*, 2007, 149, 387–398; (b) E. Ramírez, F. Recasens, M. Fernández and M. A. Larrayoz, *AIChE J.*, 2004, 50, 1545–1555.
- 38 P. H. Henna, M. R. Kessler and R. C. Larock, *Macromol. Mater. Eng.*, 2008, 293, 979–990.
- 39 J. Yoon, R. T. Mathers, G. W. Coates and E. L. Thomas, *Macromolecules*, 2006, 39, 1913–1919.
- 40 (a) D. S. Van Es, *J. Renewable Mater.*, 2013, 1, 61–72; (b) D. J. Burke, T. Kawauchi, M. J. Kade, F. A. Leibfarth, B. McDearmon, M. Wolffs, P. H. Kierstead, B. Moon and C. J. Hawker, *ACS Macro Lett.*, 2012, 1, 1228–1232.